

STUDY OF THE OXIDATION OF NICKEL IN SUB- AND SUPERCRITICAL AQUEOUS SOLUTIONS BY X-RAY ABSORPTION NEAR-EDGE STRUCTURE

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It appears that the fast propagation of the crack corrosion in supercritical aqueous middle could be due to the different regimes of solubility between sub- and supercritical conditions. According to a general agreement, the solubility of the materials and the reactivity in sub-critical conditions are of electrochemical nature and the corrosion is defined as wet corrosion. In supercritical conditions the reactivity is purely chemical and the corrosion is defined as dry corrosion. The coupling of these different mechanisms inside an initiated crack enhances the propagation of the crack inside the wall of the container. This communication reports X-ray absorption near-edge structure (XANES) results on the kinetics behaviour of the reaction of a nickel foil immersed in a aqueous solution containing different oxidising concentrations of H₂O₂ in sub critical (25 MPa and 350°C) and supercritical conditions (25 MPa and 390°C) .

INTRODUCTION

The development of the applications of the supercritical water ($T_c= 647$ K and $P_c=22$ MPa) are power plans, waste hydrothermal oxidation and chemistry. There are no real difficulties in industries using pure water. however, the strong crack corrosion of the majority of usual metallic alloys restrains the development of industrial scale applications of supercritical aqueous solutions (1-6) in chemistry. Recently there are an interest in the development of in situ techniques which allow the examination of low scale metal surfaces during the corrosion process. However, despite many measurements using a variety of techniques, it was only recently that in situ synchrotron X-ray diffraction has been used to determine the local structure and properties of thin metal films (7,8).

The transformation of nickel in contact of oxidizing aqueous solution both in sub-critical (25 MPa, 625 K) and supercritical (25 MPa, 675 K) conditions has been studied by use of a X-ray absorption near-edge structure (XANES) method. These conditions are sufficient to be sure to reach sub- and supercritical conditions in every concentration of impurity in the aqueous solution. The method allows to observe the specific action of the nearest fluid layer on the metal surface in different conditions of pressure, temperature and oxygen concentration

without intrusion of a material gauge. The available X-ray energy on the line is sufficient to pass through a 4 μm foil of nickel. The aim of this communication is to evidence the difference in the local (micron scale) behaviour between sub-critical corrosion (wet corrosion) and supercritical corrosion (dry corrosion) and to propose a thermo-chemical hypothesis for the fast propagation of the fissures in such conditions.

I - EXPERIMENTAL PART

Figure 1. shows the high pressure (40 MPa) – high temperature (680 K) optical cell. The main specificity is the use of two diamond windows ($\text{\O} 4 \text{ mm}$ and 0.5 mm thick) as pressure-

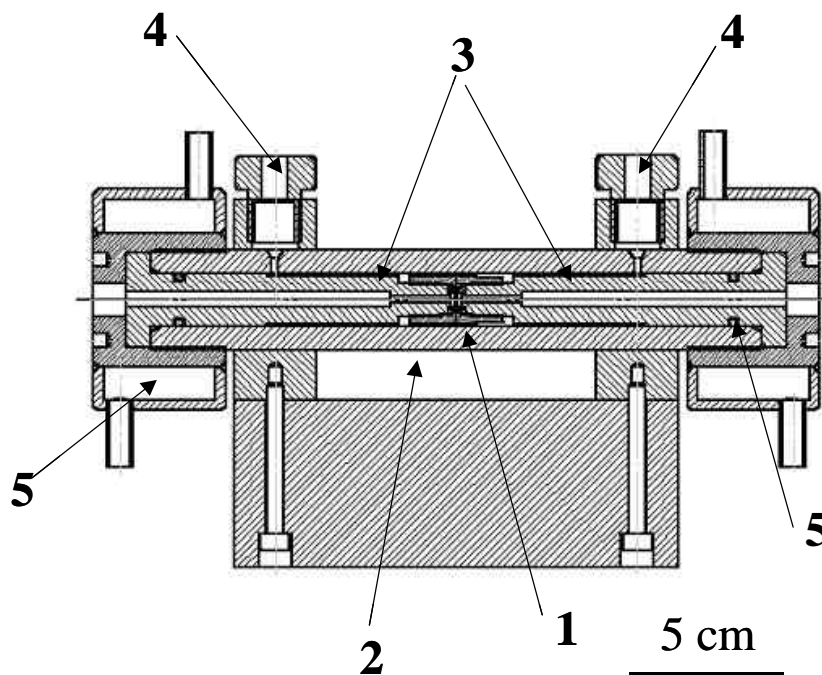


Figure 1. Optical cell: (1) sample and diamond windows, (2) position of the heater, (3) windows support, (4) fluid connexions, (5) O-ring.

tightness. The windows (synthetic polycrystalline CVD diamond) were mounted in such a way to provide a 100 μm fluid light path length. A ballast of 100 cm^3 allowed to maintain the global oxygen concentration during the experiments. The pressure is measured by a resistive gauge (Sedeme) and regulated by an automatic valve. The temperature is PID regulated and measured by a thermocouple K set in a hole in the outside wall of the pressure cartridge. A previous calibration of the temperature has been made between the external thermocouple and a thermocouple set between the two diamond windows. The pressure cartridge has been build in XN26TW steel without further protection known to its good behaviour under high temperature-high pressure water.

The samples were 4 μm pure nickel foils (Goodfellow Co.) set between the diamond windows. The aqueous solutions were mixed with different concentrations of H_2O_2 in order to simulate oxidizing solutions. Around a half an hour is necessary to achieve the stability of the temperature and pressure to begin the experiment. In the case of the high concentration of H_2O_2 the kinetics of corrosion could be affected.

The ratio I/I_0 at the nickel absorption edge (8332 eV) is $2 \cdot 10^{-2}$ taking into account the $4 \mu\text{m}$ nickel sample. Therefore the weakness of this ratio needs the use of the high photons flow of a synchrotron radiation beam. The neighbouring region of the absorption edge (XANES) of the absorption spectrum, in the range of few eV up to 50 eV, concerns the electrons whose energy is weakly higher than the energy of the threshold. The photoelectron is emitted with a kinetic energy still weak and a high free path. It is involved in multiple diffusions with the surrounding atoms. The structure of the spectrum in this region contains information on the local order around the absorbent atom and its electronic structure. This part particularly shows the change in the oxidizing states of the absorbent atom by its environment.

XANES experiments were performed in the Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE – Orsay) using the combination of X-ray energy dispersive optics and a position detector able to work under high pressure flux conditions for both in-situ and time dependent investigations. The cooled photodiode array is a unique tool which gives good spatial resolution and high dynamics. The Bragg focusing optics allows concentration of the full energy band-pass in a spot whose width is on the order of 0.5 mm or less when the high pressure cell is installed. The position sensitive detector transforms the correlation between the photon energy and the direction of the beam path of a monochromatic photon into a correlation between the photon energy and the pixel number of the detector (9,10)

II - RESULTS

The rate of transformation of a nickel foil under the action of sub-critical and supercritical aqueous solution containing 10% in weight of H_2O_2 at the beginning of the experiment are reported. Figure 2 shows the XANES of the Ni K-threshold as a function of the time for sub- and supercritical water.

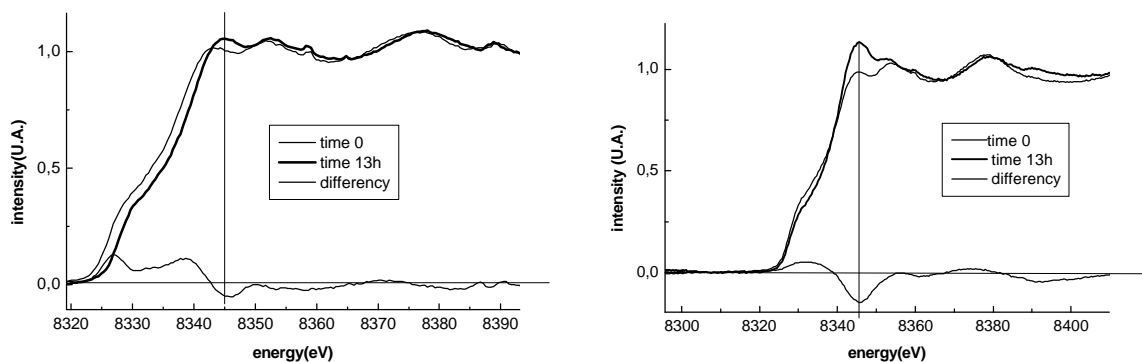


Figure 2: XANES spectra showing the difference of the rate of transformation between sub- (right) and supercritical (left) treatment of a $4 \mu\text{m}$ nickel foil (the kinetics times are 10 H)

The increase of the first oscillating structure (the so called white band (WB)) is characteristic of the formation of Ni^{2+} . The figure shows that the WB is stronger in the sub-critical condition and shows that the corrosion of Ni is more efficient in this thermodynamic region. **Figure 3** shows the results of the integration of the white band in the two conditions.

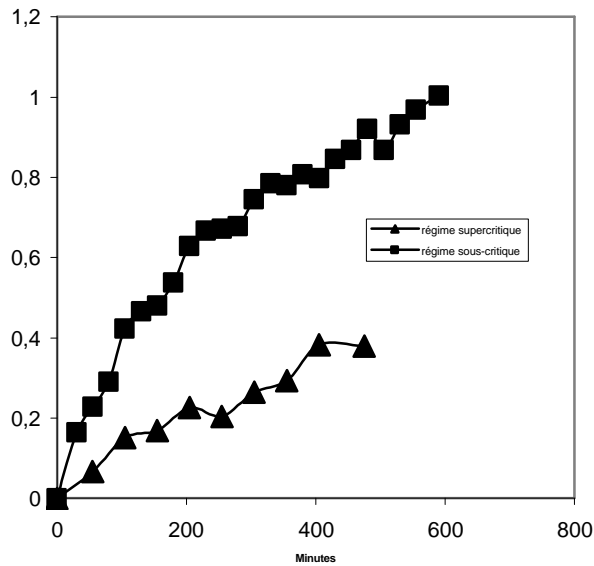


Figure 3: Integral of the white band in sub- and supercritical water versus the time

III- DISCUSSION

The **Figure 4.** shows the time concentration of nickel in the supercritical and sub-critical aqueous solution. These figures has been calculated from the combination of the XANES spectra of each pure material in room conditions (Ni, NiO (green and black) and Ni(OH)₂) measured at the Ni K-threshold to fit with the experimental XANES spectra.

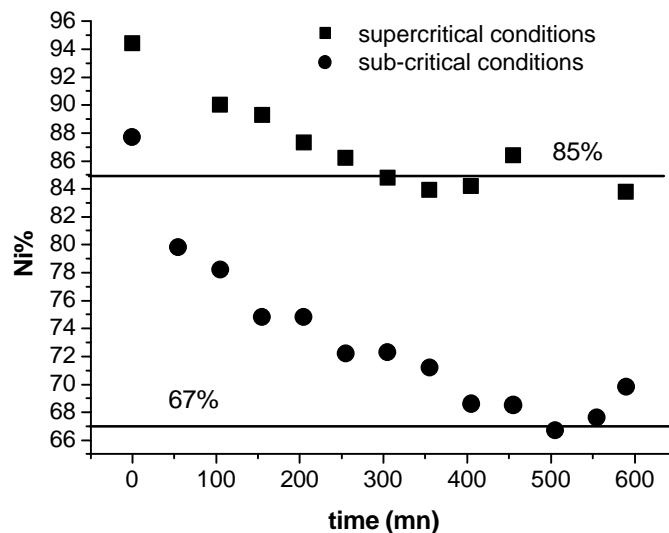


Figure 4. Lost of nickel metal versus time in sub- and supercritical conditions

This picture shows then an estimation of the lost of metal following the thermodynamics conditions (more than the half part in the sub-critical conditions and 0.6 μm in supercritical conditions for a 4 μm foil in around 5 hours).

These results allow several comments.

(1) If the metal is in contact with the aqueous solution at constant conditions of pressure, temperature and concentration in oxidizing agent, the passivity occurs after a time depending of the thermodynamic conditions. More high is the concentration of oxidizing agent more steeply appears this film. The results of different concentrations in H_2O_2 (5, 15 and 20 V%) will be report in the oral communication in comparison with the 10 V% H_2O_2 shown in the figure 2.

(2) The kinetics of reaction are strongly different in sub- and supercritical conditions (wet and dry corrosion). This difference could be the main raison of the propagation of cracks due to the fast alternation of the thermodynamics conditions at the microscopic scale of a crack (whatever its origin)..

(3) the combination of the standards to recover the final XANES spectrum of the corroded foil is an estimation. The Raman characterization of a nickel foil corroded in a sub-critical 10 V% H_2O_2 solution (Figure 5) shows that the nature of the oxide layer is not actually homogenate and more complex than the simple combination of the standard nickel oxides.

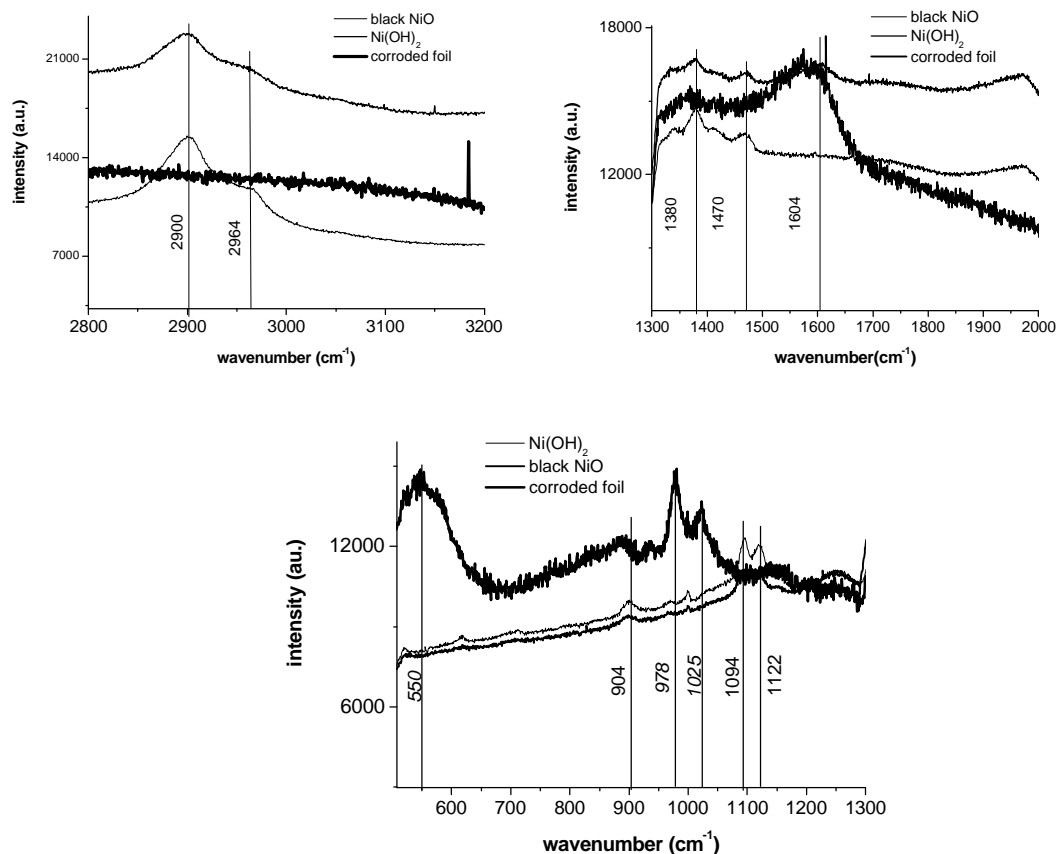


Figure 5. Raman characterization of the oxide layer on a corroded nickel foil in a sub-critical (10 V% H_2O_2) aqueous solution compared with the Raman spectra of stoichiometric NiO and $\text{Ni}(\text{OH})_2$.

CONCLUSION

This communication shows results of some experiments using XANES to characterize the locally microscopic behaviour of nickel foils in sub-and supercritical aqueous solutions. The results shows the capacity of such as method. The pursuit of this study is divided in two part.

First, the measurements will be extended to other metallic constituents and alloys used in the building of industrial reactors for high pressure-high temperature aqueous solutions. Second, thank to the measured kinetics, the modelling of the movements of the hyper-compressible solution inside the propagating fissure will allow to estimate, the propagation rate versus the thermodynamic conditions of the reactor.

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